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Effect of a micro-copolymer addition on the thermal conductivity of fly ash mortars

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Abstract

In this study, a copolymer composed of hollow spherical particles with an average particle size of 90 µm was evaluated as a lightweight aggregate in Portland cement-fly ash mortars to improve the thermal conductivity (*k*) of the composite. Mortars were produced for three different water/binder ratios by mass (*w/b*), 0.4, 0.5 and 0.6. Optimized proportions were obtained for a minimum target compressive strength of 35 kg_f/cm^2 (3.4 MPa) according to the requirements of Mexican standards for non-structural masonry units. Thermal conductivity was determined for dry and saturated samples through the transient plane technique with average results of 0.16 W/(m·K) and 0.31 W/(m·K), respectively. These values represent an increment of 23 % and a reduction of 33 %, respectively, in comparison to an efficient Portland cement-based commercially available thermal insulator.

Keywords: Thermal conductivity, fly ash, micro co-polymer, mortars.

Introduction

Thermal conductivity (k) is a material property that provides information about the rate of heat flow within a material, and is commonly used to assess the insulating potential of solid materials such as Portland cement-based composites. In Portland cement-based mortars or concretes, k will depend on the properties of the constituents. With the goal of reducing heat flow through the material, constituent materials with lower thermal conductivities should be incorporated into the mixture. In this regard, numerous researchers have investigated the incorporation of materials such as cork, expanded clay, rubber, expanded polystyrene and other lightweight materials (1, 2, 3) that have been commonly used as a partial or total replacement for normal weight aggregates. In many of these works, a clear linear trend between thermal conductivity and density was established. Other works that studied fly ash incorporation have reported a decrease of the thermal conductivity, due to its lightweight and amorphous network (4, 5, 6). Combinations of fly ash-lime have been studied for the production of autoclaved light-weight building bricks, reaching a maximum thermal conductivity of 225 W/(m·K) (7).

Recently, improvements in thermal efficiency and concurrent savings on the costs of heating/cooling have received renewed attention worldwide. For example, in the north of México, during the hot weather season, the demand for energy increases as a result of the environmental temperature conditioning required to provide comfort within living spaces (8, 9). Since an increment of air conditioning units is expected in Mexico, associations such as IPPC (10), CONAGUA (8) and INECC (11) predict a proportional energy consumption growth. To mitigate this trend, one of the feasible technological solutions consists of the evaluation of novel Portland cement-based material formulations to improve the performance of these composites as thermal insulators and contribute to improved thermal comfort. As a technologically feasible option, this paper reports the results of a research work that was performed to evaluate the effectiveness of a lightweight copolymer composed of hollow micro-spheres as a unique aggregate in a portland cement-fly ash mortar, and presents experimental results for a series of portland cement-fly ash mortars developed to meet a target specified compressive strength while improving thermal performance.

Materials and Methods

In addition to tap water, four other ingredients were used for the production of the mortars. An ASTM C 150-12 (12) Type I Ordinary Portland Cement (OPC) was used in all mixtures. An ASTM C 618-05 (13) type F fly ash (FA) was used as a supplementary cementitious material (SCM) in substitution of the Portland cement (PC) in a majority of the mixtures. A copolymer (COP) with particle sizes between 10 µm and 200 µm was used as a unique aggregate in the composite (see figure 1). Finally, an ASTM C494-09 polycarboxylate-based high-range water-reducing admixture (HRWRA) was used in every mortar series to maintain similar consistencies and paste dosages as the water-to-binder ratio (*w/b*) decreases. Table 1 presents some of the key properties for the characterization of the different ingredients used for the production of the mortars involved in this study; from this table, one can highlight the low density of the COP (120 kg/m^3) and the lower thermal conductivity that represents 4 % of the *k* for OPC and 5 % of the *k* for FA.

Table 1. Properties of materials.

Material	Density, (kg/m^3)	Strength activity index	Average particle size, (µm)	Thermal Conductivity, [W/(m·K)]
OPC	3.03	-----	20	1.050
FA	2.02	78 %	70	0.816
COP	120	-----	90	0.043
SP	1090	-----	-----	-----

A total of 13 mixtures with different volume contents of co-polymer were made to determine their compressive strength and to select those that meet the requirements of the Mexican specification for structural masonry units (14). From these thirteen mixtures, six mortars with mixture parameters within the ranges of study for *w/b*, fly ash and copolymer contents were selected for thermal conductivity determinations. A commercial cellular concrete was also evaluated as a commercially available reference material for this study.

Thermal conductivity was determined on twin cylindrical specimens with a diameter of 80 mm and a height of 20 mm through the transient plane source technique (15), with an equipment that uses a 30 mm Kapton 5501 hot disk sensor and the following setup: power of 0.8 W, test time of 80 s, and measurement depth in the range of 7 mm to 10 mm. Thermal conductivity was calculated based on the transient heat flow from the sensor into the twin specimens (15, 16). Samples were analyzed under two different humidity conditions; 24 h oven-dried samples at 100 °C after 7 d of standard curing, and wet samples immersed in distilled water for 24 h. Tests were performed using samples isolated from the environment (inside of a sealed plastic bag) during the duration of the measurement in a room with a temperature of 23 °C ± 1 °C and relative humidity ≥ 50 %.

For compressive strength determinations, 50 mm x 50 mm x 50 mm standard cubes were produced according to ASTM C 109-05 (17); all the specimens were cured in standard conditions (23 °C ± 1 °C and RH ≥ 95 %) until the age of their testing.

Table 2 presents identification labels and proportions for all of the thirteen mixtures considered in this study; numbers 1, 2 and 3 represent the three different *w/b* ratios (0.6, 0.5 and 0.4); A, B and C represent the three different copolymer contents in percentage of the total mixture volume and CV1 to CV4 identifies the fly ash mass substitutions as a percentage of the total cementitious content.

The process to optimize the copolymer and fly ash content initiated with a *w/b* of 0.6, and had a target minimum compressive strength of 35 kgf/cm^2 (3.4 MPa) to meet the Mexican standard for non-structural masonry units (14). In order to maximize the proportions of these two ingredients, another two set of mortars with *w/b* ratios of 0.4 and 0.5 were produced.

Results and Discussion

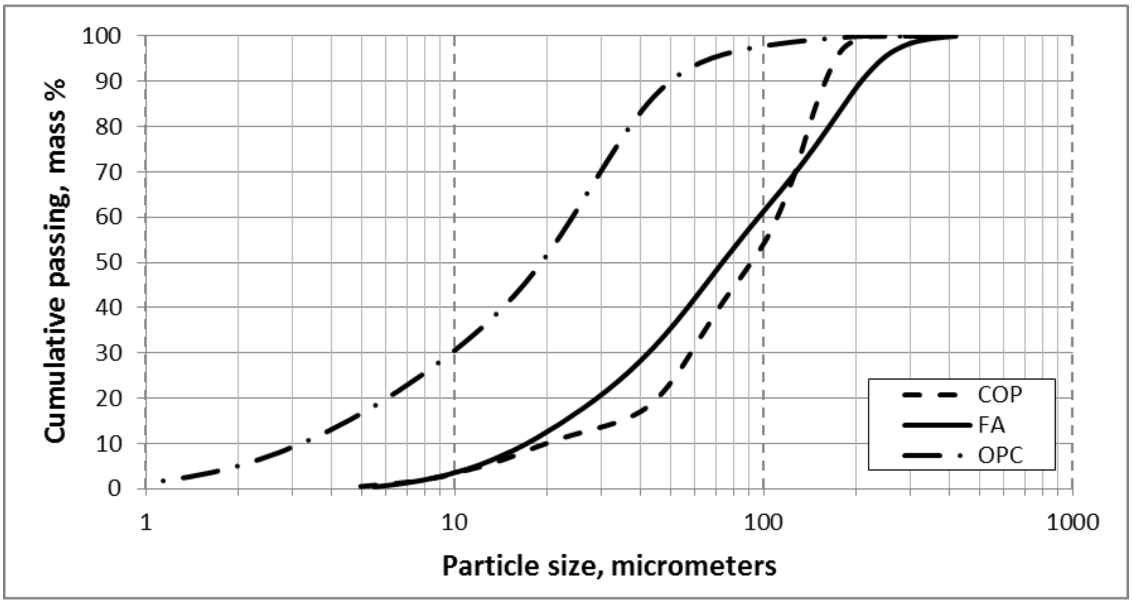
Materials characterization

Particle size distributions (PSD) of OPC, FA and COP were obtained by laser diffraction and are reported in the Figure 1. Results illustrate that FA and COP have a similar PSD and that both are coarser than OPC. Properties including thermal conductivity, density and average particle size for OPC, FA, and COP are reported in the Table 1.

Table 2. Mixture identification and proportions.

<table>
<tr><th>Identification</th><th>w/b</th><th>Fly ash substitution (% by mass of cement)</th><th>Co-polymer (% of total volume)</th></tr>
<tr><td>1A</td><td rowspan="5">0.6</td><td>-</td><td rowspan="5">43</td></tr>
<tr><td>1A-CV1</td><td>25</td></tr>
<tr><td>1A-CV2</td><td>35</td></tr>
<tr><td>1A-CV3</td><td>45</td></tr>
<tr><td>1A-CV4</td><td>55</td></tr>
<tr><td>2A-CV2</td><td rowspan="4">0.5</td><td rowspan="4">35</td><td>43</td></tr>
<tr><td>2B-CV2</td><td>45</td></tr>
<tr><td>2C-CV2</td><td>47</td></tr>
<tr><td>2D-CV2</td><td>50</td></tr>
<tr><td>3A-CV2</td><td rowspan="4">0.4</td><td rowspan="4">35</td><td>43</td></tr>
<tr><td>3B-CV2</td><td>45</td></tr>
<tr><td>3C-CV2</td><td>47</td></tr>
<tr><td>3D-CV2</td><td>50</td></tr>
<tr><td>H</td><td colspan="3">Cellular concrete</td></tr>
</table>

Figure 1. Particle size distributions of OPC, FA and COP.



The particle morphologies presented in Figure 2 indicate that FA and COP are generally spherical in shape. Figures 3 and 12a indicate that the copolymer particles are hollow, a characteristic that confirms their low thermal conductivity reported in Table 2 and that suggests their potential positive contribution to decrease the thermal conductivity of cement-based materials.

Figure 2. Particle morphology for OPC (a), FA (b) and COP (c).

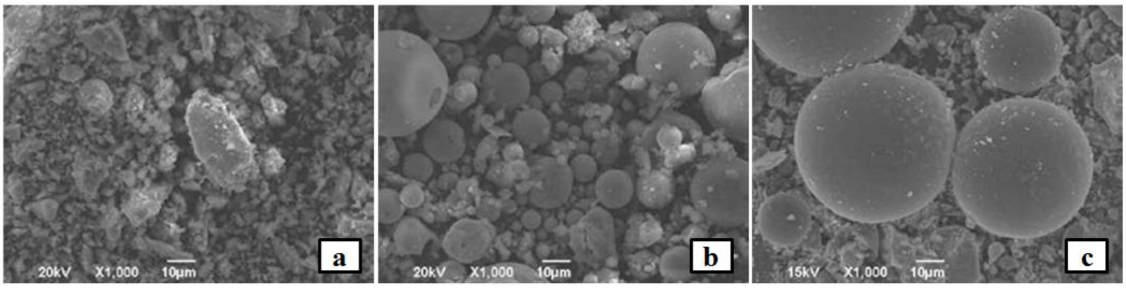
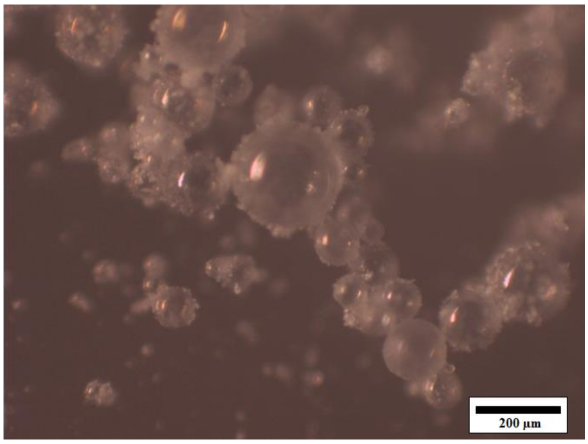


Figure 3. Particle morphology of COP.



Fresh stage properties

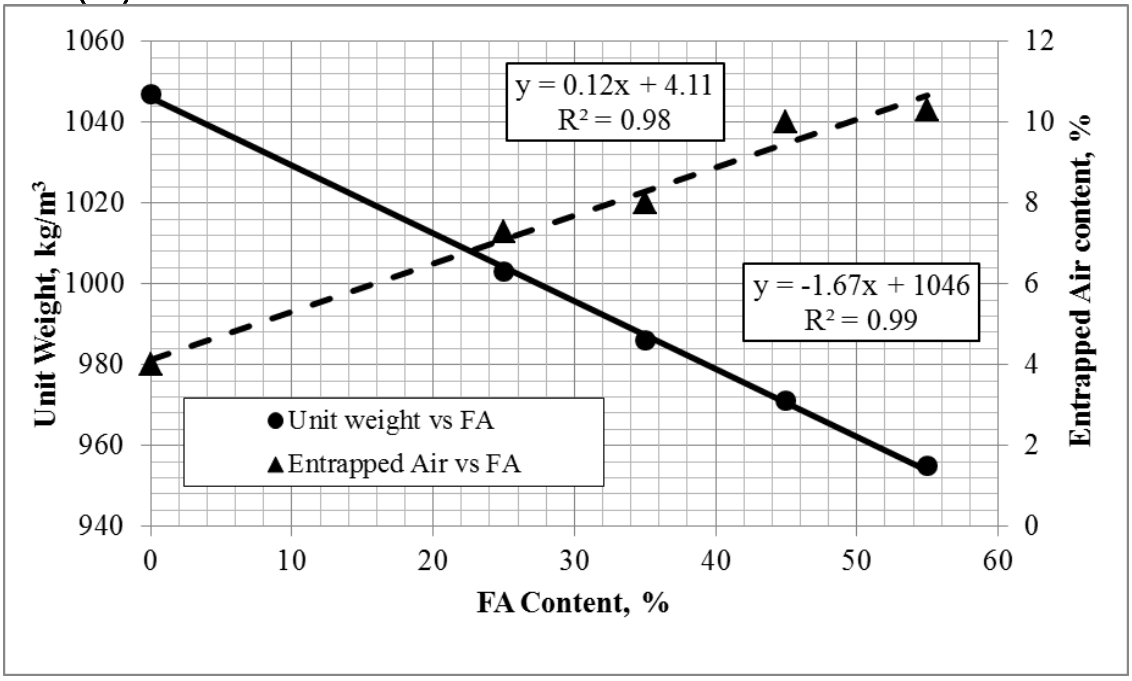
Fresh stage characterization of mortars considered flow (ASTM C230-07) and unit weight-entrapped air determinations (ASTM C185-01). Results of single determinations are reported in Table 3. For these methods, the precision and bias section of the standard procedures reported that the single-operator, within-laboratory standard deviation has been found to be 4 % for flow and 0.56 % for air content through the range of 8 % to 19 % air, respectively. No uncertainty is provided in the ASTM standard for unit weight measurements.

For each copolymer dosage, a cement paste fraction was fixed, and to obtain an appropriate consistency, which could facilitate the fabrication of specimens, a high-range water-reducing admixture (HRWRA) was used. HRWRA was also used to improve the rheological properties of the mortars when the *w/b* decreases or the fly ash and/or copolymer increases. Variations in cohesiveness as a result of the previously mentioned factors or their combination led to flows in the range of 71 % to 132 %, as reported in Table 3. For *w/b* of 0.6, and a COP content of 43 % by volume (A), Figure 4 illustrates that as fly ash increases from 0 % to 55 % by mass of cement, the unit weight decreases from 1047 kg/m^3 to 955 kg/m^3 and the air content increases from 4.8 % to 10.3 %.

Table 3. Fresh stage properties

Identification	Flow (%)	Unit Weight, (kg/m^3)	Entrapped air, (%)
1A	132	1047	4.00
1A-CV1	127	1003	7.30
1A-CV2	110	986	8.00
1A-CV3	96	971	10.00
1A-CV4	73	955	10.30
2A-CV2	130	1012	7.90
2B-CV2	120	981	11.20
2C-CV2	121	950	12.60
2D-CV2	71	902	13.30
3A-CV2	109	1053	7.30
3B-CV2	100	1019	8.40
3C-CV2	72	987	9.90
3D-CV2	62	937	12.50

Figure 4. Effect of FA substitutions on unit weight and air content of fresh mortars with w/b 1 (0.6).



Figures 5 and 6 present the same correlations for the second (0.5) and third (0.4) *w/b*, respectively, both for a fixed fly ash content CV2 (35 %). For COP contents between 43 % and 50 % by volume, Figure 5 illustrates that as COP increases by 1 %, unit weight decreases by 15.7 kg/m^3 and air content increases by 0.7 %. Figure 6 illustrates that average values of 16.5 kg/m^3 and 0.75 % were produced for the third *w/b* (0.4), respectively.

Figure 5. Effect of COP substitutions on the unit weight and air content of fresh mortars with w/b 2 (0.5).

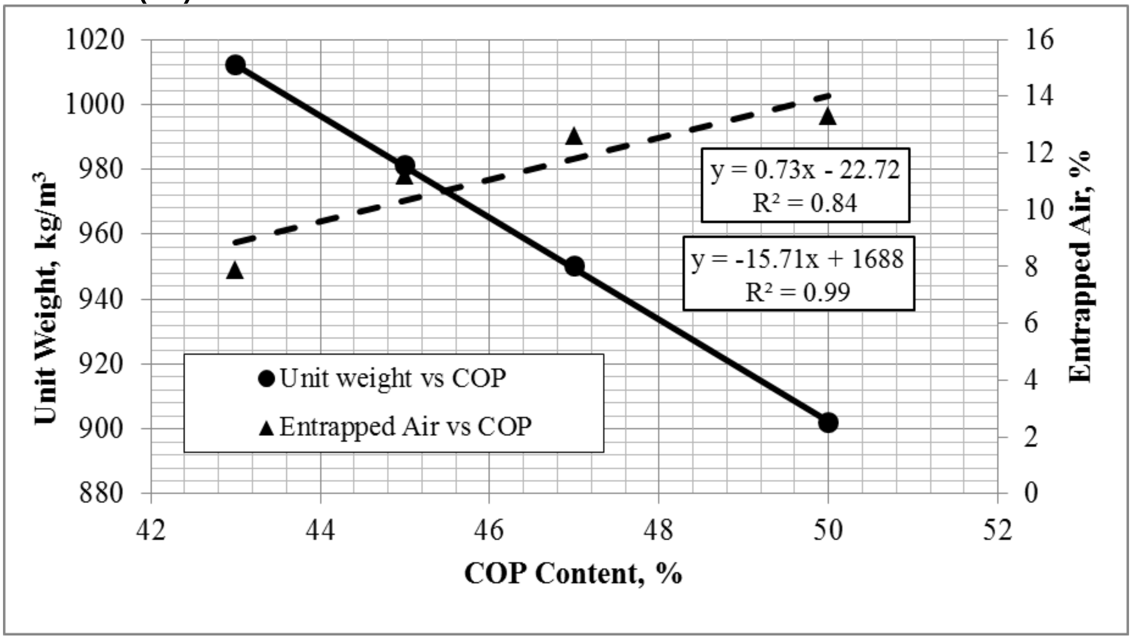
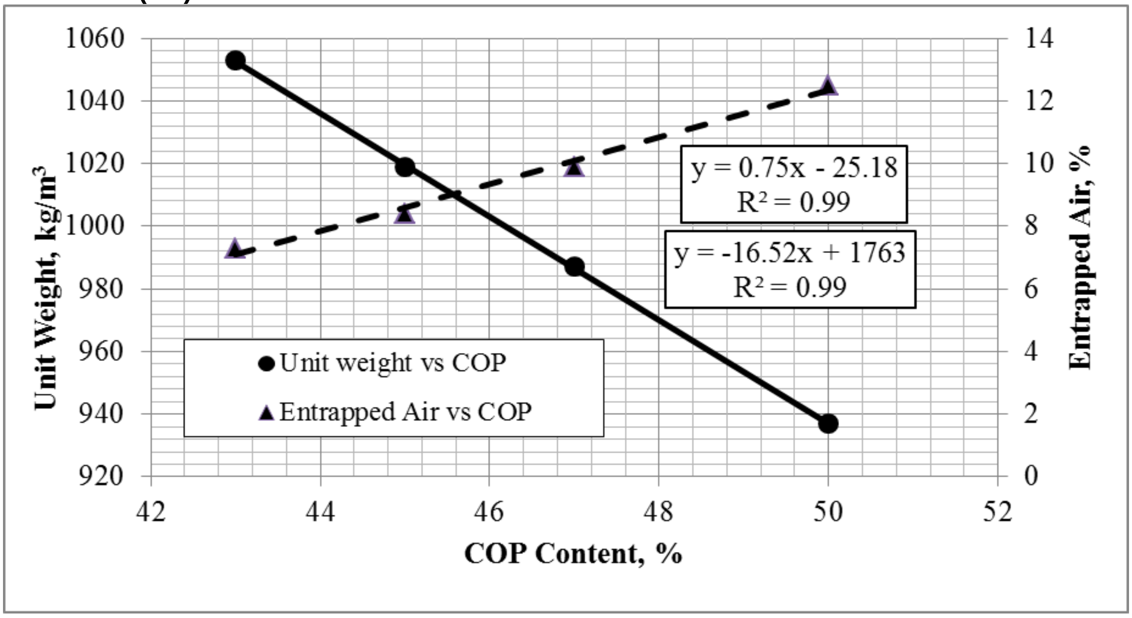


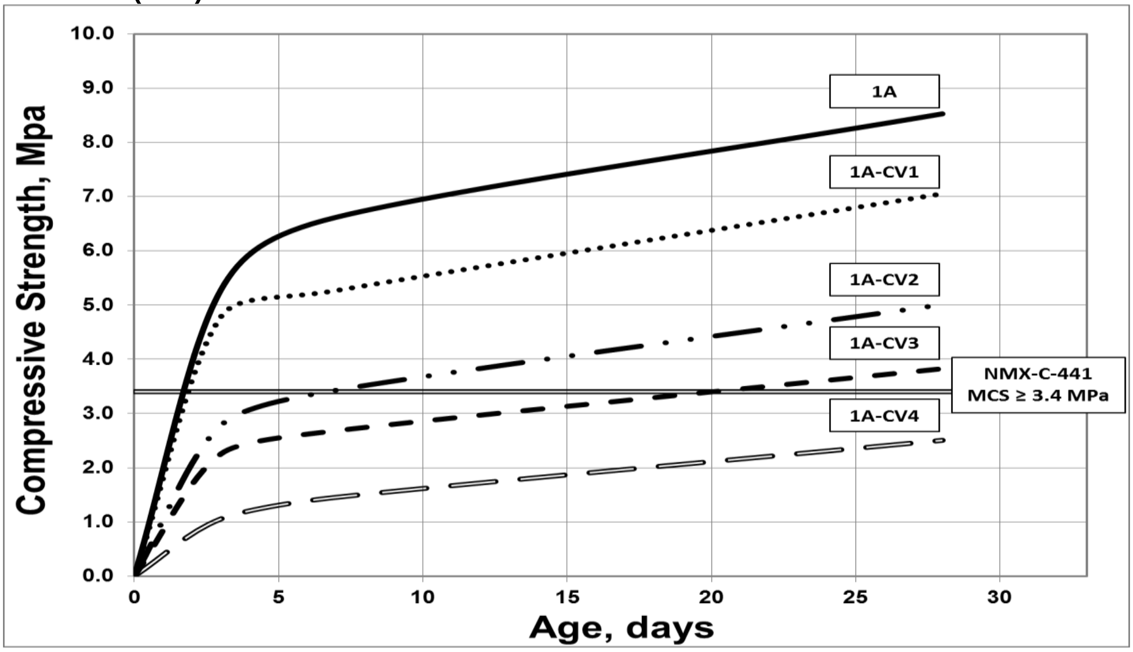
Figure 6. Effect of COP substitutions on the unit weight and air content of fresh mortars with w/b 3 (0.4).



Compressive strength

The minimum compressive strength (MCS) of 35 kgf/cm^2 (3.4 MPa) required by NMX C441 (14) was fixed to determine the maximum substitution of cement by fly ash, for a fixed copolymer dosage of 43 % by volume (COP A); for this purpose, a set of five mortars with fly ash substitutions of 0 %, 25 %, 35 %, 45 % and 55 % were produced. Because fast track industrial applications are the main potential to transfer this technology for practical applications, the required age to meet target strengths for optimization purposes was fixed at 7 d. Figure 7 indicates that mixtures with CV1 and CV2 satisfy this requirement. Thus, a fly ash substitution of 35 % (CV2) was fixed for later stages of the optimization process.

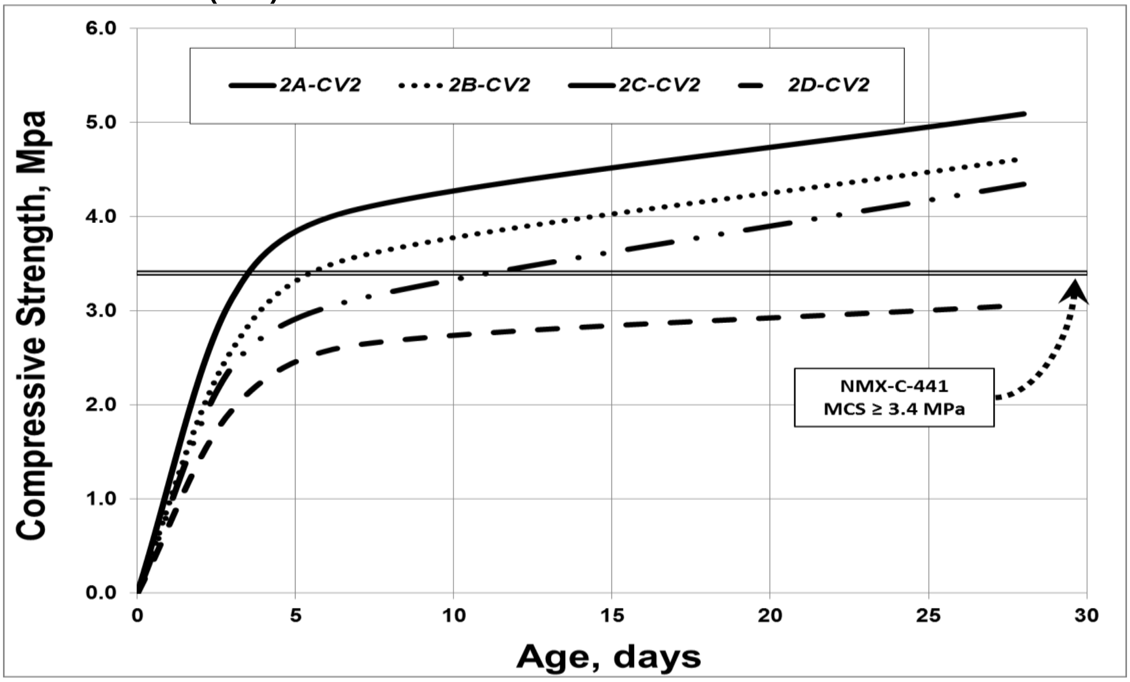
Figure 7. Effect of FA on compressive strength mixtures with w/b 1 (0.6) and COP content A (43%).



For a fixed FA substitution of 35 %, Figures 8 and 9 present the compressive strength results for *w/b*´s of 0.5 and 0.4, respectively, and for COP volumes of 43 %, 45 %, 47 % and 50 %. For *w/b*=0.5, results illustrate that a COP content between 43 % and 47 % can be used to obtain MCS at ages between 4 d and 12 d, and for *w/b*=0.4, results illustrate that mixtures with COP contents between 43 % and 47 % meet the minimum compressive strength at an age of 3 d and that a COP content of 50 % by volume meets this requirement at an age of 20 d. From all the mixtures that meet the minimum target compressive strength, a set of six mixtures with *w/b* and

COP contents within the ranges studied in this project were selected for thermal conductivity evaluations.

Figure 8. Effect of COP content on compressive strength of mixtures with w/b 2 (0.5) and FA content CV2 (35%).



All of the standard deviations for the compressive strengths reported in Figures 7, 8 and 9 were generally within the range of variations permitted by ASTM C 109 (8.7 % for three cubes and 7.6 % for two cubes). For each average result (set of 3 or 2 cubes), the standard errors calculated as an estimate of the uncertainty for the observations in regards to the estimation of the average compressive strength were within the following ranges: 0.81 % to 10.02 % for *w/b*=0.6 and COP A (Figure 7), 0.29 % to 12.22 % for *w/b*=0.5 and CV2 (Figure 8) and 0.08 % to 13.54 % for *w/b*=0.4 and CV2 (Figure 9).

Thermal conductivity

Figure 10 presents the results of thermal conductivity measurements with values in the range of 0.168 W/(m·K) to 0.225 W/(m·K) and 0.317 W/(m·K) to 0.377 W/(m·K) for the six samples in dry or water saturated conditions, and yielding an average of 0.190 W/(m·K) and 0.341 W/(m·K) for dry and wet conditions, respectively. Estimations reported in Figure 10 are the average of three observations, with the variation among the individual readings for a specimen usually being within the 2 % reproducibility reported by the equipment manufacturer. Specifically, for water-saturated and dry samples, the standard error of the average estimations for the thermal conductivities reported in figure 10 were within the following ranges, from 0.26 % to 2.04 % and from 0.42 % to 1.85 %, respectively.

Figure 9. Effect of COP content on compressive strength of mixtures with w/b 3 (0.4) and FA content CV2 (35%).

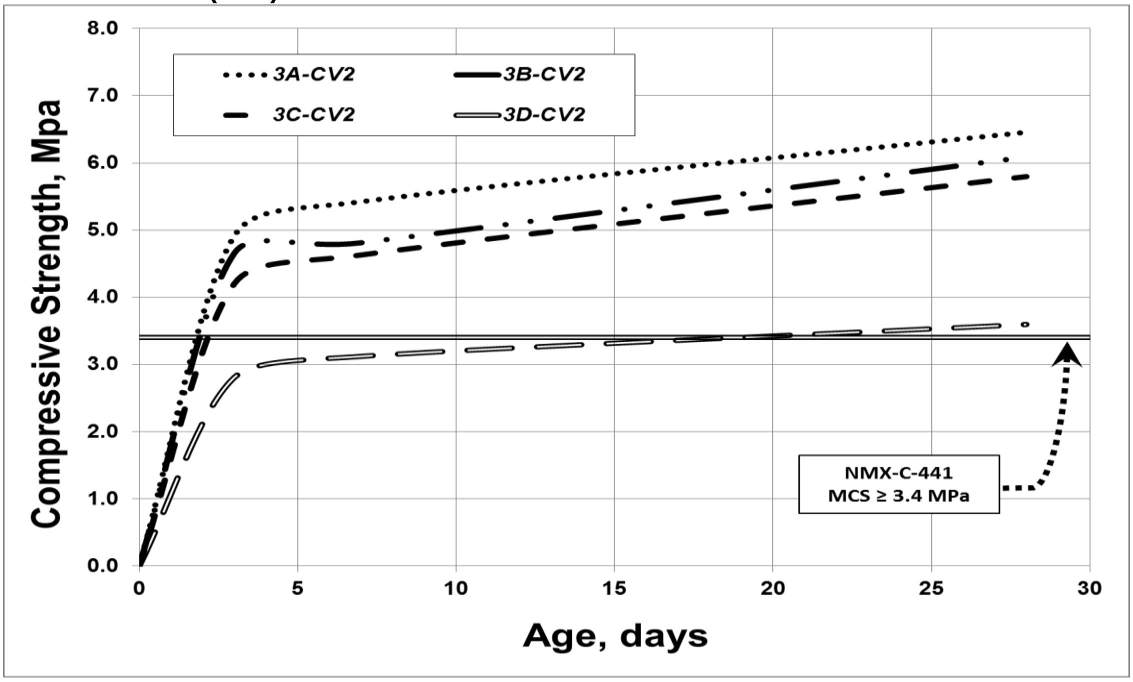
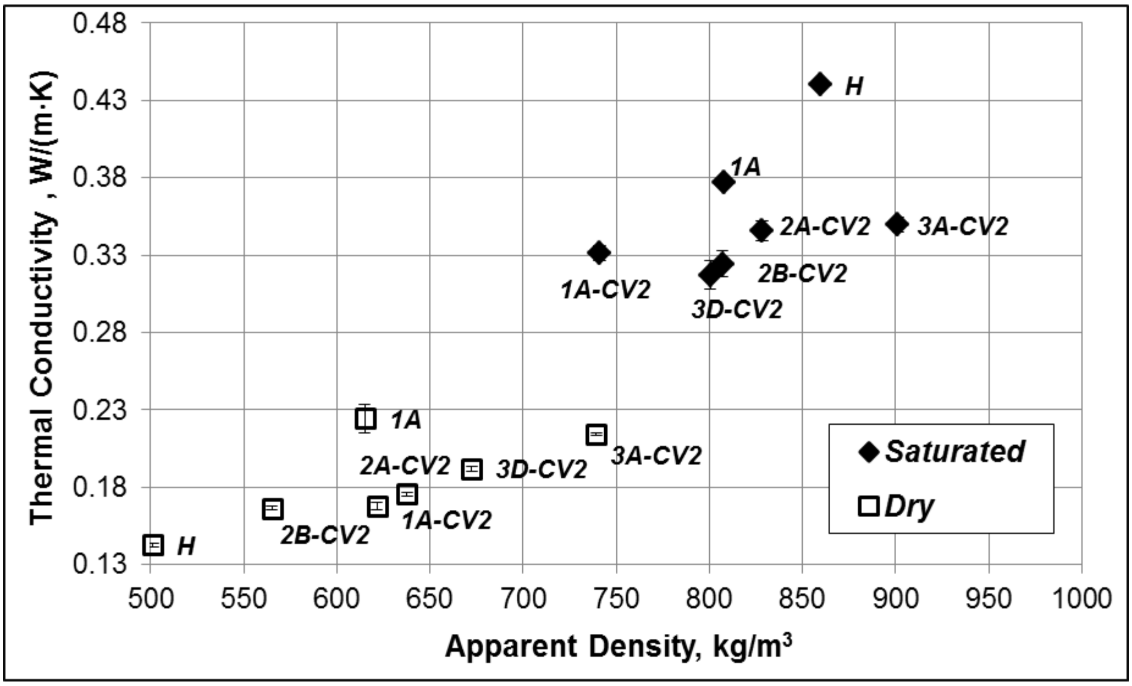


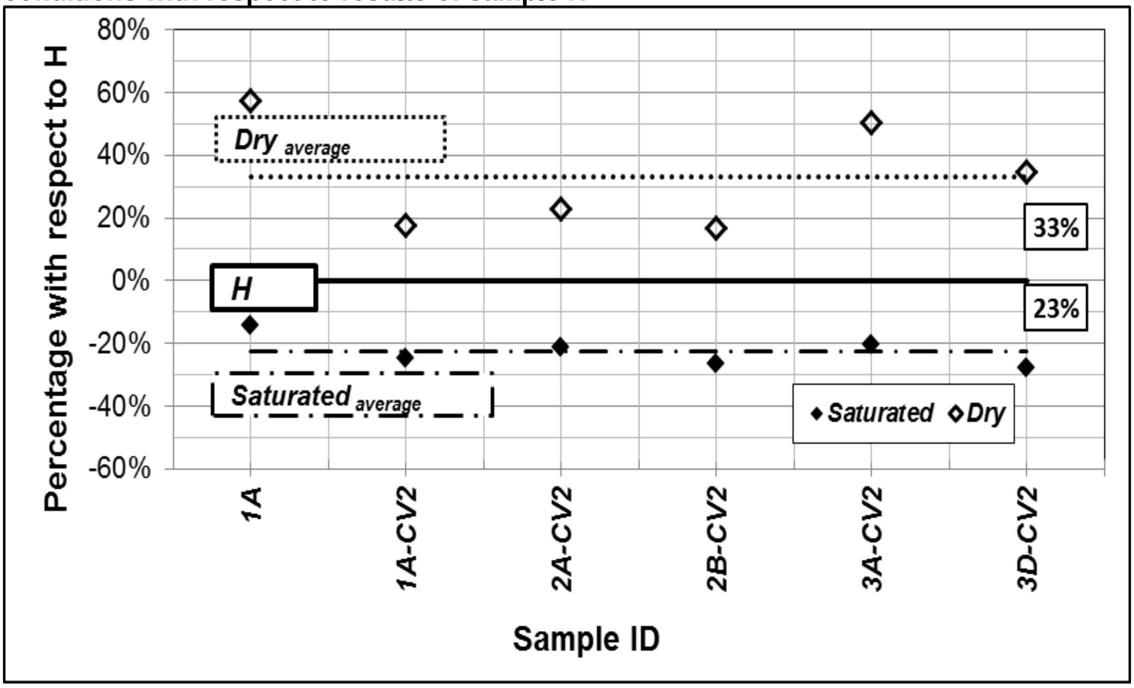
Figure 10. Thermal conductivities of COP and sample H mortars in dry or water-saturated conditions.



Results illustrate the adverse influence of water regarding the thermal properties of a Portland cement-based composite; an average increment of 79.5 % can be attributed to the presence of the water within the pore and crack network of the material. For comparing thermal conductivities for samples 1A and 1A-CV2 in dry and water-saturated conditions, the incorporation of fly ash contributed to improve (reduce) *k* by 23 % and 13 %, respectively.

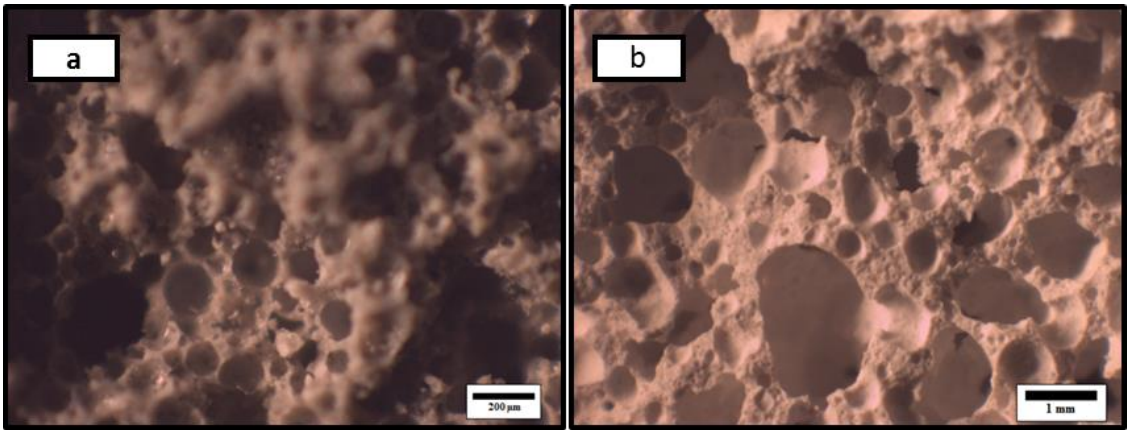
For the same humidity conditions, sample H presents *k* values of 0.143 W/(m·K) and 0.440 W/(m·K) for dry and water saturated conditions, respectively, in Figure 10. In comparison to *k* obtained for sample H, Figure 11 presents the average *k* results for COP mortars in dry and water-saturated conditions. Results illustrate that on average, COP mixtures in a water saturated condition can lead to 23 % lower conductivities than sample H, and conversely to an increment of 33 % for samples in dry conditions.

Figure 11. Average thermal conductivity of COP mixtures in dry or water-saturated conditions with respect to results of sample H.



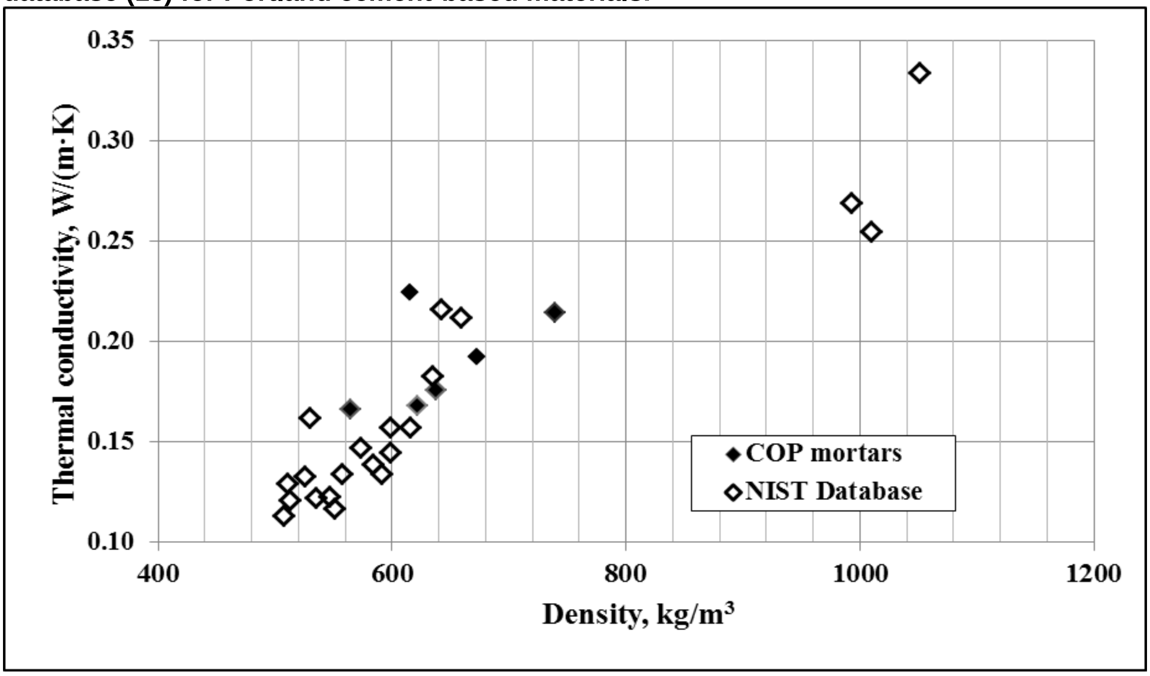
The microstructure observed in Figure 12 indicates a uniform network of spherical voids in the COP mortars. In figures 10 and 12, COP mixtures in saturated condition exhibit a lower thermal conductivity than sample H; this is attributed to the waterproofing benefit provided by the shell of the copolymer spheres that prevents saturation of the COP particles when the mortar is saturated.

Figure 12. Optical micrographs of COP mortar (a) and sample H mortar (b).



Thermal conductivities of COP mixtures are in general agreement with the results published in the database established by NIST (18) for Portland cement-based light-weight materials (Figure 13). Similarly, consistent correlations have been reported for pumice light-weight concrete, with densities between 1329 kg/m^3 and 2270 kg/m^3 and thermal conductivities between 0.78 W/(m·K) and 1.46 W(m·K) respectively and for recycled aggregate concrete with densities between 1617 kg/m^3 and 2195 kg/m^3 and thermal conductivities between 0.81 W/(m·K) and 1.40 W(m·K) respectively (19, 20). Both of these materials exhibit higher densities, and correspondingly higher thermal conductivities, than the COP mixtures investigated in the present study.

Figure 13. Comparison of thermal conductivities of COP mixtures with those in the NIST database (18) for Portland cement-based materials.



Conclusions

The results of this work indicate the potential for a specific copolymer in improving thermal conductivity when used as an ingredient in Portland cement-based composites, for the production of non-structural masonry systems, and that the formulations evaluated exhibit a performance similar to a commercial cellular concrete. Results also confirm the beneficial contribution of fly ash in improving the thermal conductivity of these composites and confirm consistent *k* vs density correlations, as reported previously.

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